

WHAT IS CLAIMED IS:

1. A polymer microsphere comprising at least one polymer and at least one bound latent colorant, wherein said microsphere is stabilized by at least one stabilizing polymer.

2. The polymer microsphere of claim 1 wherein said at least one polymer comprises a water insoluble polymer.

3. The polymer microsphere of claim 1 wherein said polymer comprises an addition polymer made from at least one monomer comprising α,β -ethylenic unsaturation.

4. The polymer microsphere of claim 3 wherein said monomer comprises a monomer having limited solubility in water.

5. The polymer microsphere of claim 3 wherein said monomer comprises at least one member selected from the group consisting of styrenic, acrylic ester, or methacrylic ester.

6. The polymer microsphere of claim 1 wherein said at least one polymer comprises at least two monomers.

7. The polymer microsphere of claim 6 wherein said at least two monomers comprise at least one water insoluble monomer and at least one water soluble monomer.

8. The polymer microsphere of claim 6 wherein said at least one water soluble monomer comprises less than 10% of the total polymer microsphere weight.

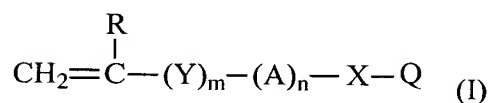
9. The polymer microsphere of claim 6 wherein said at least one water soluble monomer comprises from 0 to 2% of the total polymer microsphere weight.

10. The polymer microsphere of Claim 1 wherein said latent colorant comprises a latent colorant covalently bound to said microsphere.

11. The polymer microsphere of claim 1 wherein said latent colorant comprises a latent colorant polymerized into said microsphere.

12. The polymer microsphere of claim 1 wherein said latent colorant comprises at least one coupler.

13. The polymer microsphere of claim 12 wherein said at least one coupler comprises formula (I):



wherein:

R represents a hydrogen atom, a lower alkyl group containing from 1 to 4 carbon atoms, or a chlorine atom;

X represents --CONH--, --NHCONH--, --NHCOO--, --COO--, --SO₂--, --CO-- or --O--; Y represents --CONH-- or --COO--;

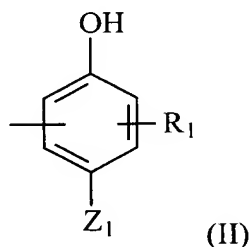
A represents an unsubstituted or substituted alkylene group containing from 1 to 10 carbon or an unsubstituted or substituted phenylene group;

Q represents a cyan color forming coupler residue, a magenta color forming coupler residue or a yellow color forming coupler residue capable of forming a dye upon coupling with an oxidation product of an aromatic primary amine developing agent;

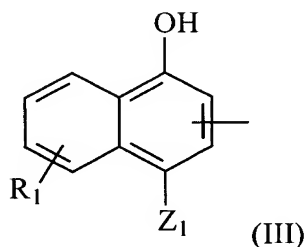
m represents 0 to 1; and

n represents 0 or 1.

14. The polymer microsphere of claim 13 wherein Q comprises a cyan color forming coupler phenol type residue represented by the general formula (II):



or a cyan color forming coupler naphthol type residue represented by the general formula (III):



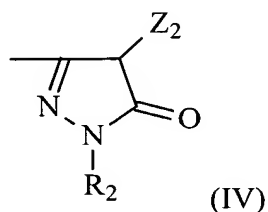
wherein:

R_1 independently comprises a hydrogen atom, an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxycarbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group, an arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamido group or an arylureido group; and

Z_1 comprises a hydrogen atom, a halogen atom, or a substituted or unsubstituted sulfo group, acyloxy group, alkoxy group, aryloxy group, heterocyclic oxy group, alkylthio group, arylthio group or heterocyclic thio group.

15. The polymer microsphere of claim 13 wherein said Q comprises a magenta color forming coupler pyrazolone type residue and a magenta color forming coupler indazolone type residue.

16. The polymer microsphere of claim 13 wherein said Q comprises a magenta color forming coupler residue having formula (IV):

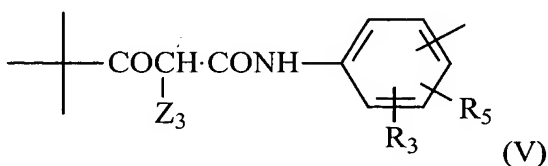


wherein:

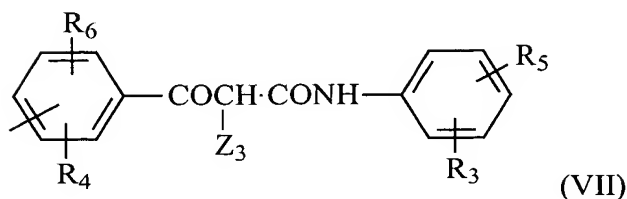
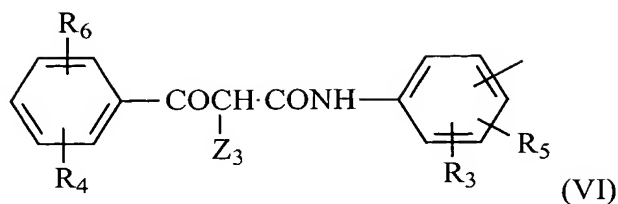
R_2 comprises a substituent at the 1-position of a 2-pyrazolin-5-one coupler, a substituted alkyl group, an aryl group or a substituted aryl group; and

Z_2 comprises a hydrogen atom, a nitrogen atom, a sulfur atom, or a releasing group connected to the coupling position of the color forming coupler through an oxygen atom.

17. The polymer microsphere of claim 13 wherein said Q comprises a yellow color forming coupler acylacetanilide type residue, a yellow color forming coupler pivaloylacetanilide type residue represented by the general formula (V): or



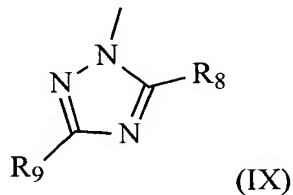
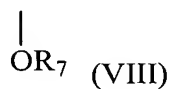
a yellow color forming coupler benzoylacetanilide type residue represented by the general formula (VI) or (VII):

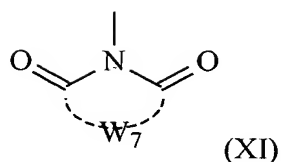
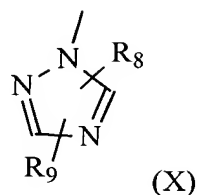


wherein:

R_3 , R_4 , R_5 and R_6 each independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxycarbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group, an alkyl substituted succinimido group, an aryloxy group, an aryloxycarbonyl group, an arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamido group, an arylureido group, a carboxy group, a sulfo group, a nitro group, a cyano group or a thiocyano group;

Z_3 in the general formula comprises a hydrogen atom or a group represented by the general formula(VIII), (IX), (X) or (XI):



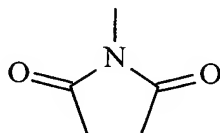


wherein:

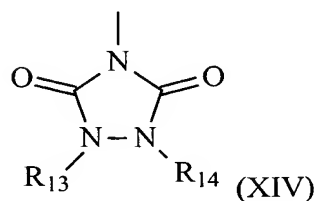
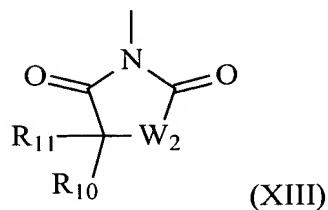
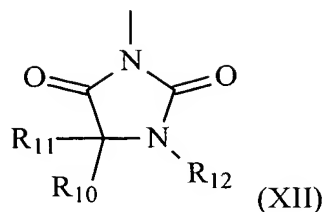
R₇ represents an unsubstituted or substituted aryl group or an unsubstituted or substituted heterocyclic group;

R₈ and R₉ each independently represents a hydrogen atom, a halogen atom, a carboxylic acid ester group, an amino group, an alkyl group, an alkylthio group, an alkoxy group, an alkylsulfonyl group, a carboxylic acid group, a sulfonic acid group, an unsubstituted or substituted aryl group or an unsubstituted or substituted heterocyclic group; and

W₇ represents non-metallic atoms necessary to form a 4-membered ring, a 5-membered ring or a 6-membered ring together with



18. The polymer microsphere of claim 17 wherein said groups represented by general formula (XI) comprise at least one member selected from the groups consisting of a group is represented by the following formulas (XII),(XIII) or (XIV):



wherein:

R_{10} and R_{11} each independently represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group or a hydroxy group;

R_{12} , R_{13} and R_{14} each independently represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or an acyl group; and

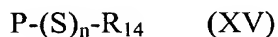
W_2 represents an oxygen atom or a sulfur atom.

19. The polymer microsphere of claim 12 wherein said latent color couplers comprise photographic couplers.

20. The polymer microsphere of claim 12 wherein said couplers are made from a polymerizable ethylenically unsaturated monomer.

21. The polymer microsphere of claim 20 wherein said polymerizable ethylenically unsaturated monomer comprises at least one member selected from the group consisting of methacrylate esters, acrylate esters, acrylamides, and methacrylamides.

22. The polymer microsphere of claim 1 wherein said latent colorant comprises at least one photochromic monomer having the following structure (XV):



wherein:

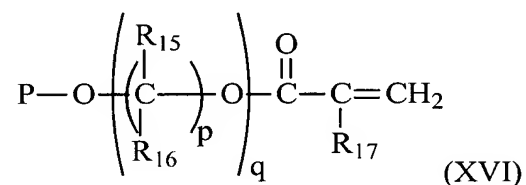
n is an integer of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

S is an organic spacer group; and

R₁₄ is a polymerizable group.

23. The polymer microsphere of claim 22 wherein said photochromic material comprises at least one reacted photochromic monomer having the formula (XVI):



wherein:

P is a photochromic dye derivative from a photochromic dye selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides;

q is an integer of 0 to 5;

p is an integer of 1 to 10;

R₁₅ and R₁₆ are independently selected from hydrogen, halogen and an alkyl or substituted alkyl of 1 to 10 carbon atoms, an aryl or heterocyclic group of 5 to 10 carbon atoms; and

R₁₇ is selected from hydrogen, halogen, alkyl or substituted alkyl of 1 to 10 carbon atoms or alkoxy, or substituted alkoxy or 1 to 10 carbon atoms.

24. The microsphere of claim 1 wherein said latent colorant comprises at least one thermochromic colorant.

25. The microsphere of claim 1 wherein said latent colorant comprises at least one metal complex colorant.

26. The microsphere of claim 1 wherein said latent colorant comprises at least one metal complex colorant.

27. The microsphere of claim 1 wherein said latent colorant comprises a leuco dye.

28. The microsphere of claim 27 wherein said leuco dye comprises polymerizable ethylenic unsaturation.

29. The microsphere of claim 1 wherein said stabilizing polymer comprises a linear polymer.

30. The microsphere of claim 1 wherein said stabilizing polymer comprises a soluble polymer.

31. The microsphere of claim 30 wherein said soluble stabilizing polymer comprises a polymer soluble in water or water miscible solvent.

32. The microsphere of claim 1 wherein said microsphere comprises an external surface and said stabilizing polymer is bound to said external surface of said microsphere.

33. The microsphere of claim 32 wherein said stabilizing polymer is covalently grafted, chemisorbed, or physically adsorbed to said external surface of said microsphere.

34. The microsphere of claim 1 wherein said stabilizing polymer comprises at least one member selected from the group consisting of poly(vinylamine), poly(propyleneimine), poly(N-aminopropyl methacrylamide), polyacrylic acid, or polymethacrylic acid.

35. The microsphere of claim 1 wherein said stabilizing polymer contains at least one chemically reactive group.

36. The microsphere of claim 35 wherein said at least one chemically reactive group comprises a carboxylic acid, primary amine, secondary amine, tertiary amine, thiol, alcohol, vinylsulfone)

37. The polymer microsphere of claim 1 wherein said stabilizing polymer comprises a molecular weight of from 500 to 1,000,000 AMU.

38. The polymer microsphere of claim 1 wherein said stabilizing polymer comprises a molecular weight of from 5,000 to 250,000 AMU.

39. The microsphere of Claim 1 wherein said microsphere comprises an average diameter from 1 – 100 microns.

40. The microsphere of Claim 1 wherein said microsphere comprises an average diameter from 2 to 30 microns.

41. The microsphere of Claim 1 wherein said microsphere comprises an average diameter from 3 to 20 microns.

42. The microsphere of Claim 1 wherein said microsphere comprises an addition polymer microsphere.

43. The microsphere of claim 1 wherein said microsphere is monodisperse.

44. The microsphere of claim 43 wherein said monodisperse microsphere comprises a diameter having a coefficient of variation of less than 20%.

45. The microsphere of claim 1 wherein further comprising a tag bound to the external surface of said microsphere.

46. The microsphere of claim 1 wherein said tag comprises a bioaffinity tag.

47. The microsphere of claim 46 wherein said bioaffinity tag is covalently bound to the microsphere.

48. The microsphere of claim 46 wherein said bioaffinity tag is bound to said stabilizing polymer.

49. The microsphere of claim 46 wherein said bioaffinity tag comprises at least one member selected from the group consisting of polynucleotides, polypeptides, polysaccharides, nucleic acids, antigens, enzymes, antibodies, and proteins.

50. A method of preparing polymer microspheres comprising combining at least one latent colorant, at least one ethylenically unsaturated monomer, a stabilizing polymer, and an initiator in at least one solvent and initiating polymerization to form a polymeric microsphere stabilized by a stabilizing polymer bound to the external surface of said polymeric microsphere.

51. The method of claim 50 wherein said polymer comprises an addition polymer made from at least one monomer comprising α,β -ethylenic unsaturation.

52. The method of claim 51 wherein said monomer comprises a monomer having limited solubility in water.

53. The method of claim 51 wherein said monomer comprises at least one member selected from the group consisting of styrenic, acrylic ester, methacrylic ester.

54. The method of claim 50 wherein said at least one monomer comprises at least two monomers.

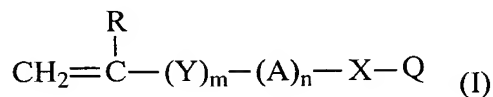
55. The method of claim 50 wherein said polymer comprises a molecular weight of from 500 to 1,000,000 AMU.

56. The method of Claim 50 wherein said latent colorant comprises a latent colorant covalently bound to said microsphere.

57. The method of claim 50 wherein said latent colorant comprises a latent colorant polymerized into said microsphere.

58. The method of claim 50 wherein said latent colorant comprises at least one coupler.

59. The method of claim 58 wherein said at least one coupler comprises formula (I):



wherein:

R represents a hydrogen atom, a lower alkyl group containing from 1 to 4 carbon atoms, or a chlorine atom;

X represents --CONH--, --NHCONH--, --NHCOO--, --COO--, --SO₂--, --CO-- or --O--; Y represents --CONH-- or --COO--;

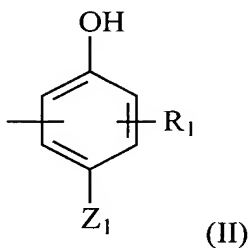
A represents an unsubstituted or substituted alkylene group containing from 1 to 10 carbon or an unsubstituted or substituted phenylene group;

Q represents a cyan color forming coupler residue, a magenta color forming coupler residue or a yellow color forming coupler residue capable of forming a dye upon coupling with an oxidation product of an aromatic primary amine developing agent;

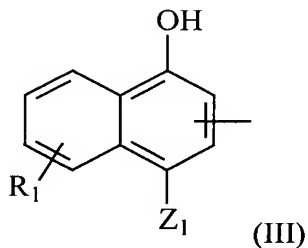
m represents 0 to 1; and

n represents 0 or 1.

60. The method of claim 59 wherein Q comprises a as a cyan color forming coupler phenol type residue represented by the general formula (II):



or a as a cyan color forming coupler naphthol type residue represented by the general formula (III):



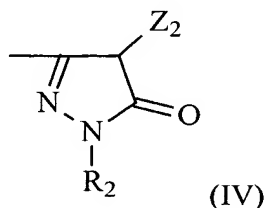
wherein:

R₁ independently comprises a hydrogen atom, an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxycarbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group, a arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamido group or an arylureido group; and

Z₁ comprises a hydrogen atom, a halogen atom, or a substituted or unsubstituted sulfo group, acyloxy group, alkoxy group, aryloxy group, heterocyclic oxy group, alkylthio group, arylthio group or heterocyclic thio group.

61. The method of claim 59 wherein said Q comprises a magenta color forming coupler pyrazolone type residue and a magenta color forming coupler indazolone type residue.

62. The method of claim 59 wherein said Q comprises a magenta color forming coupler residue having formula (IV):

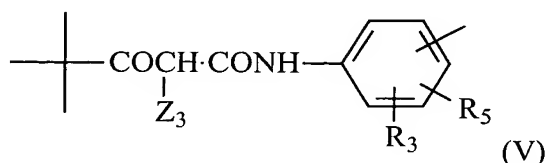


wherein:

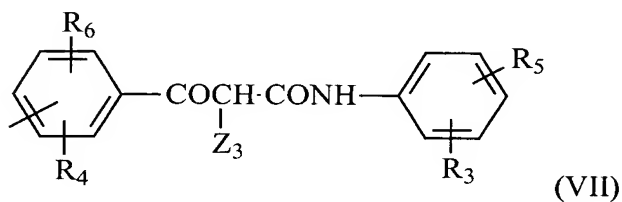
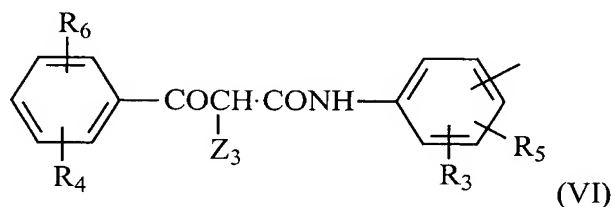
R₂ comprises a substituent at the 1-position of a 2-pyrazolin-5-one coupler, a substituted alkyl group, an aryl group or a substituted aryl group; and

Z₂ comprises a hydrogen atom, a nitrogen atom, a sulfur atom, or a releasing group connected to the coupling position of the color forming coupler through an oxygen atom.

63. The method of claim 59 wherein said Q comprises a yellow color forming coupler acylacetanilide type residue, a yellow color forming coupler pivaloylacetanilide type residue represented by the general formula (V): or



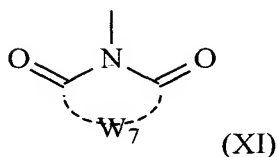
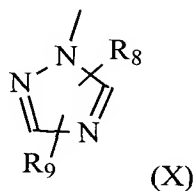
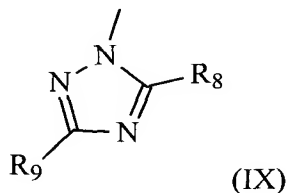
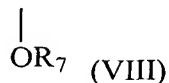
a yellow color forming coupler benzoylacetanilide type residue represented by the general formula (VI) or (VII):



wherein:

R_3 , R_4 , R_5 and R_6 each independently represents a hydrogen atom, an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxycarbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group, an alkyl substituted succinimido group, an aryloxy group, an aryloxycarbonyl group, an arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamido group, an arylureido group, a carboxy group, a sulfo group, a nitro group, a cyano group or a thiocyno group;

Z₃ in the general formula comprises a hydrogen atom or a group represented by the general formula(VIII), (IX), (X) or (XI):

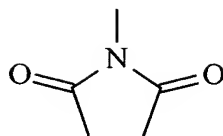


wherein:

R₇ represents an unsubstituted or substituted aryl group or an unsubstituted or substituted heterocyclic group;

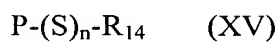
R₈ and R₉ each independently represents a hydrogen atom, a halogen atom, a carboxylic acid ester group, an amino group, an alkyl group, an alkylthio group, an alkoxy group, an alkylsulfonyl group, a carboxylic acid group, a sulfonic acid group, an unsubstituted or substituted aryl group or an unsubstituted or substituted heterocyclic group; and

W₇ represents non-metallic atoms necessary to form a 4-membered ring, a 5-membered ring or a 6-membered ring together with



64. The method of claim 50 wherein said latent color couplers comprise photographic couplers.

65. The method of claim 50 wherein said latent colorant comprises at least one photochromic monomer having the following structure (XV):



wherein:

n is an integer of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

S is an organic spacer group; and

R₁₄ is a polymerizable group.

66. The method of claim 50 wherein said latent colorant comprises at least one thermochromic colorant.

67. The method of claim 50 wherein said latent colorant comprises at least one metal complex colorant.

68. The method of claim 50 wherein said latent colorant comprises at least one leuco dye.

69. The method of claim 68 wherein said leuco dye comprises polymerizable ethylenic unsaturation.

70. The method of claim 50 wherein said stabilizing polymer comprises a linear polymer.

71. The method of claim 50 wherein said stabilizing polymer comprises a soluble polymer.

72. The method of claim 50 wherein said microsphere comprises an external surface and said stabilizing polymer is bound to said external surface of said microsphere.

73. The method of claim 50 wherein said bound stabilizing polymer is covalently grafted, chemisorbed, or physically adsorbed to said external surface of said microsphere.

74. The method of Claim 50 wherein said microsphere comprises an average diameter from 1 – 100 microns.

75. The method of Claim 50 wherein said microsphere comprises an addition polymer microsphere.

76. The method of claim 50 wherein said microsphere is monodisperse.

77. The method of claim 76 wherein said monodisperse microsphere comprises a diameter having a coefficient of variation of less than 20%.

78. The method of claim 50 wherein further comprising a bioaffinity tag bound to the surface of said microsphere.

79. The method of claim 50 wherein said solvent comprises water, 2-methoxyethanol, methanol or ethanol.

80. The method of claim 50 wherein said polymer microsphere is insoluble in said solvent.

81. The method of claim 50 wherein said initiator is selected from the group consisting of azo compounds, organic peroxides, organic hydroperoxides, persulfate salts, and redox initiators.

82. The method of claim 50 wherein said initiator comprises an azo compound or an organoperoxide.

83. The method of claim 50 wherein said initiating polymerization comprises heating.

84. The method of claim 83 wherein said heating comprises a temperature from 35C to 85C.

85. The method of claim 83 wherein said heating comprises a temperature at which said initiator initiates polymerization.

86. The method of claim 50 further comprising purifying said polymer microspheres.

87. The method of claim 50 further comprising binding a tag to the external surface of said microsphere.

88. The method of claim 87 wherein said tag comprises a bioaffinity tag.